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PERSPECTIVE

Controlling Eutrophication along the Freshwater–Marine Continuum: Dual Nutrient (N and P) Reductions are Essential

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Abstract Expanding human activities along the freshwater to marine continuum of coastal watersheds increasingly impact nutrient inputs, nutrient limitation of primary production, and efforts to reduce nutrient over-enrichment and eutrophication. Historically, phosphorus (P) has been the priority nutrient controlling upstream freshwater productivity, whereas nitrogen (N) limitation has characterized coastal waters. However, changing anthropogenic activities have caused imbalances in N and P loading, making it difficult to control eutrophication by reducing only one nutrient. Furthermore, upstream nutrient reduction controls can impact downstream nutrient limitation characteristics. Recently, it was suggested that only reducing P will effectively control eutrophication in both freshwater and coastal ecosystems. However, controls on production and nutrient cycling in estuarine and coastal systems are physically and chemically distinct from those in freshwater counterparts, and upstream nutrient management actions (exclusive P controls) have exacerbated N-limited downstream eutrophication. Controls on both nutrients are needed for long-term management of eutrophication along the continuum.

Keywords Nutrient limitation · Nitrogen · Phosphorus · Eutrophication · Freshwater to marine continuum · Water quality

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Introduction

Human population growth, urbanization, and agricultural and industrial expansion are causing unprecedented and alarming rates of nutrient over-enrichment and accelerated plant growth in receiving waters worldwide. Key nutrients of concern are nitrogen (N) and phosphorus (P) because the supply rates of these nutrients most often control or "limit" aquatic plant primary production and biomass formation. Maintaining fertility at the base of the food web is essential for productive, resourceful, and healthy aquatic ecosystems. However, nutrient over-enrichment promotes accelerated production of plant-based organic matter (i.e., eutrophication) to the extent that excessive production, including harmful algal blooms, fuels expanding zones of bottom water hypoxia (dead zones), and leads to fisheries habitat destruction, translating into ecological and economic losses of impacted waters (Nixon 1995; Boesch et al. 2001; Rabalais and Turner 2001; Diaz and Rosenberg 2008).

The negative consequences of eutrophication have been apparent in freshwater habitats for centuries, as witnessed in the detailed landscape paintings of the Dutch masters as early as the seventeenth century (Fig. 1). Early research in freshwater systems identified phosphorus (P) as a key nutrient controlling primary production (Likens 1972). The primary reason for P limitation of freshwater streams, lakes, reservoirs, and rivers is that these systems are generally supported by large watershed areas, which capture, accumulate, and mobilize relatively large amounts of biologically available N relative to P (Wetzel 2001; Peierls et al. 1991). There are exceptions however; lakes with small watersheds relative to their size or volume tend to show higher frequencies of N or N and P co-limitation (Lewis and Wurtzbaugh 2008).

Fig. 1 "River landscape", a painting by Salomon van Ruysdael (ca. 1648) depicting the eutrophic waterways of the Netherlands in the seventeenth century. Note the agricultural and human sources of nutrients and scums (presumably algal blooms) present on the water surface

In some aquatic ecosystems, biologically available N (as NH_3) can be supplied endogenously through microbial nitrogen (N_2) fixation. This capability has been used to support the argument that P will ultimately be the limiting nutrient, since N_2 fixation represents an avenue for helping satisfy N requirements under these circumstances (Doremus 1982; Tyrell 1999). Moreover, inorganic and organic forms of N are often more soluble and hence more available than P (Gunnars and Blomqvist 1997; Wetzel 2001), potentially exacerbating P limitation. Indeed, there are numerous examples of freshwater ecosystems in which P input controls have effectively controlled primary production and successfully arrested the unwanted symptoms of eutrophication (Likens 1972; Smith 1990, 2003). However, there are also examples of large lake systems (especially those with relatively small watersheds) in which N plays a key role as a limiting nutrient (Goldman 1988; Lewis and Wurtzbaugh 2008).

Downstream estuarine and coastal waters are physically, chemically, and biologically distinct from freshwater ecosystems and, as a result, their responses to nutrient inputs and over-enrichment can contrast those observed in freshwater ecosystems (Paerl 1997; Smith 2003; Howarth and Marino 2006; Bianchi 2007). Physically, water supplies and circulation are controlled by the interactive effects of basin morphology, freshwater discharge, and tidal mixing and, as a result, hydrodynamic properties of estuaries and coastal systems, including advection and stratification, flushing, and residence times, can differ markedly from freshwater systems. Geochemically, estuarine and coastal ecosystems are rich repositories of minerals derived from watershed geological (erosional) and biological (plant production, microbial and higher trophic level cycling) processes. As discussed below, these differences strongly influence the types and spatiotemporal extent of nutrient limitation, and they form the rationale for reducing both N and P inputs in order to control estuarine and coastal eutrophication.

The Rationale for a Dual Nutrient Strategy

When considering the need for nutrient controls on estuarine and coastal eutrophication, it is important to recognize that there are major distinctions between N and P cycling as these nutrients are transported to and transformed in estuarine and coastal systems. The N cycle contains diverse and abundant gaseous forms in addition to dissolved and particulate forms, while the P cycle is dominated by non-gaseous dissolved and particulate forms. This means that fractions of the N pool can exchange with and escape to the atmosphere, while P is essentially "trapped" in receiving marine waters. Processes controlling N exchange with the atmosphere include ammonification, denitrification, nitrous and nitric oxide production, products of the anammox reaction, and nitrogen (N_2) fixation (Codispoti et al. 2001; Rich et al. 2008). Of these processes, the first five represent "losses", while the latter process represents a "gain" in terms of influx and efflux of N in marine waters. No analogous air–water exchanges exist in the P cycle. The net effect of the microbially mediated dissolved gaseous fluxes on N is loss of N to the atmosphere, while P remains in the system, either as dissolved or as particulate forms.

Assuming no human influence, the result of this imbalance is increases in P relative to N accumulation along the freshwater to marine "continuum". In shallow estuarine and coastal ecosystems, this translates into an increased tendency for N limitation to occur and persist. Indeed, field, experimental, empirical, and paleoecological

evidence supports this conclusion (Fisher et al. 1988, 1999; Nixon 1995; Granéli et al. 1999; Paerl et al. 1999; Boesch et al. 2001; Conley 2000; Cloern 2001; Elmgren and Larsson 2001; Howarth and Marino 2006; Brush 2009) (Fig. 2). In pelagic ocean environments, N limitation has been shown to prevail (Dugdale 1967; Capone et al. 2008), although there are anthropogenically N-enriched near-shore regions where other nutrient limitations have been observed, most notably of silicon (Si) and P (Dortch and Whitledge 1992; Conley 2000; Sylvan et al. 2006). In addition, open ocean waters can exhibit N and iron (Fe) or exclusive Fe-limited conditions (Martin et al. 1994; Paerl et al. 1994).

In a recent study, based on 37 years of data from whole lake (Lake 227; experimental lakes area, Northwestern Ontario, Canada) experimental nutrient addition work, Schindler et al. (2008) proposed that "eutrophication of lakes cannot be controlled by reducing nitrogen input".

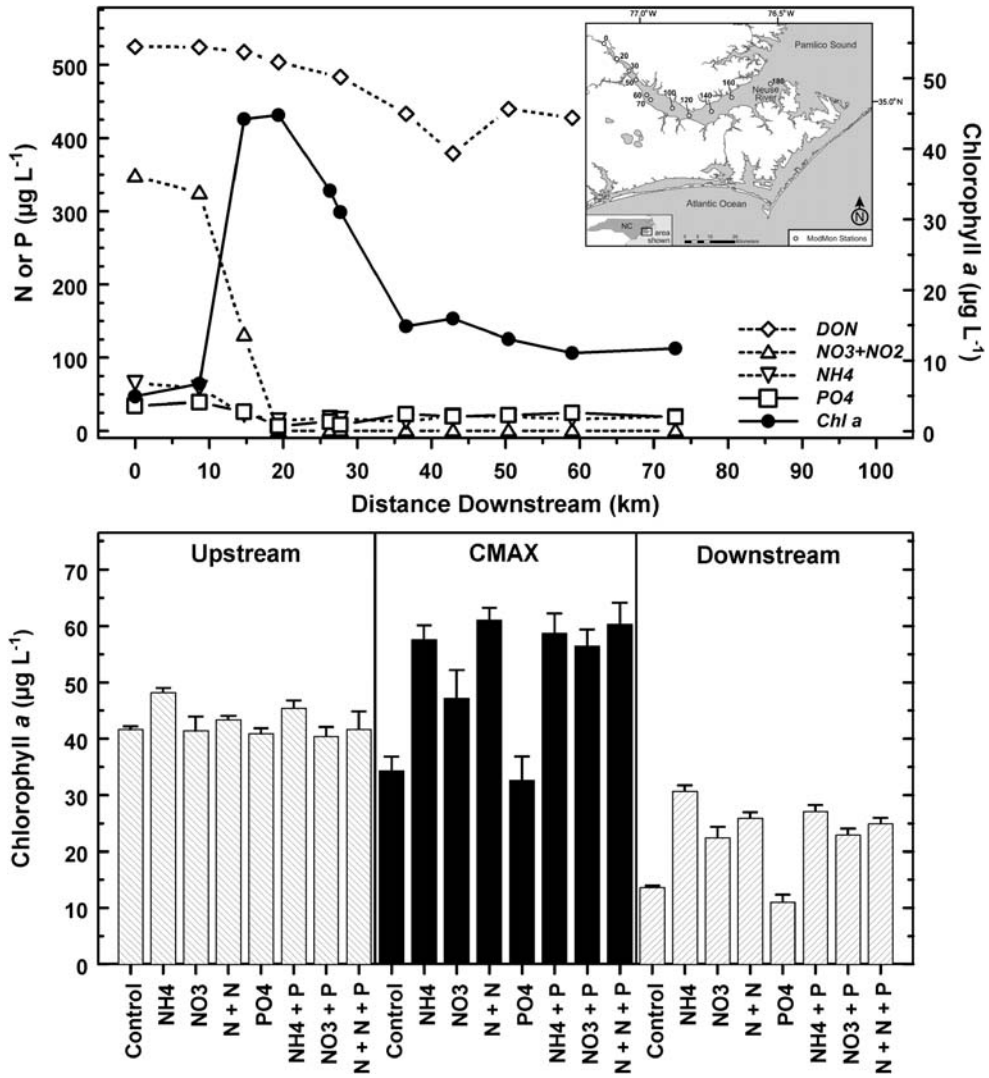

Fig. 2 Results from a set of in situ nutrient addition bioassays conducted at three locations along the axis of the Neuse River Estuary (NRE), NC, USA, that illustrate increasing N limitation along the axis of the estuary going from upstream oligohaline to downstream mesohaline conditions. Concentrations of various forms of dissolved inorganic N (nitrate + nitrite, ammonium) and dissolved organic N concentrations and chlorophyll *a*, as an indicator of phytoplankton biomass, are shown along a set of stations that are sampled biweekly. Note the steep decline in dissolved inorganic NO_3^- + NO_2^- and to a lesser extent NH_4 concentrations going downstream, especially below the mid-estuarine chlorophyll *a* maximum (*CMAX*). Dissolved inorganic P (PO_4^{-3}) concentrations remained relatively constant along the axis of the NRE, indicating sufficiency (no P limitation). In the bioassays, all nitrogen forms were added at 140 µg L^{-1} N, while phosphate was added at 40 µg L^{-1} P. The locations of bioassays were "upstream" at 10 km, "CMAX" at 25 km, and "downstream" at 50 km downstream from the head of the estuary. Strong N limitation was encountered at the CMAX location. Downstream of CMAX, N limitation dominated. Figure adapted from Paerl and Piehler (2008). Error bars indicate standard deviation among quadruplicate treatments

They also expanded this argument to estuarine and coastal waters. The Lake 227 data set is among the most extensive and lengthiest in existence, and it has yielded highly significant insights into lake responses to nutrient manipulations (Schindler et al. 1973). However, the conclusions put forth in this paper are based on a somewhat narrow perspective on biogeochemical cycling and eutrophication dynamics and a lack of consideration of the physical–chemical and biological constraints on the ability of N_2-fixing microorganisms to meet ecosystem-level nitrogen requirements along the freshwater to marine continuum. Lastly, remote Lake 227 has not been significantly impacted by anthropogenic nutrient enrichment, other than experimental manipulations. In contrast to this isolated "lake in a bubble", many, if not a great majority, of other freshwater, estuarine, and coastal ecosystems have been radically altered by human "nutrification" over the past century (c.f. Likens 1972; D'Elia et al. 1986; Paerl 1988; Nixon 1995; Vitousek et al. 1997; Boesch et al. 2001), to the extent that they behave differently from the highly controlled Lake 227. While Lake 227 has, over the past few decades, received continual doses of P (but not N), many coastal systems have experienced ever-increasing N loads from rapidly growing human sources, with severe negative impacts on ecosystem structure and function (Boesch et al. 2001; Diaz and Rosenberg 2008; Paerl and Piehler 2008). This has led to a call for N input constraints, which is warranted and scientifically defensible for the reasons provided below.

In their studies, which were initiated in 1969, Schindler at al. (2008) initially administered N and P and conclusively showed that fertilization with these nutrients greatly enhanced primary production and algal biomass (Schindler et al. 1973). The N/P fertilization ratio (by weight) was ~12. Dual nutrient fertilization was continued until the mid to late 1980s, when N fertilization was initially reduced and then discontinued while P fertilization was maintained. This led to a change in the N/P loading ratio of less than 5 once N loading was discontinued. Under this final scenario, nutrient stoichiometry conditions became increasingly favorable for N_2 fixing cyanobacterial populations to develop (c.f. Smith 1990). Indeed, given the lake's highly favorable N/P ratio, as well as its physically favorable conditions for diazotrophic cyanobacterial growth and bloom potentials (strong vertical stratification, high degree of water column stability, leading to consistent upper water column heating during the summer months) (Paerl et al. 2001), N_2-fixing cyanobacterial blooms predictively developed (Schindler et al. 2008). In this physically favorable environment, the maintenance of chemically favorable conditions (low N/P ratios) has resulted in the continuation of the summer blooms.

Schindler et al. (2008) have extrapolated these N_2 fixation responses within this chemically and physically ideal lake ecosystem to freshwater systems in general. They also argue that similar biotic responses can be expected in estuarine and coastal systems (i.e., N_2 fixation will assume a greater share of N input) without presenting supporting experimental documentation. The "take home message" from Schindler et al. (2008) is that, because N_2 fixation can respond to meet ecosystem N requirements in a regime of P enrichment, P ultimately controls eutrophication and the need for N input controls is obviated.

However, this argument for single (P) nutrient input reductions to control eutrophication is idealized and conceptually and technically inapplicable to many freshwater and marine ecosystems. While Lake 227 is far removed from anthropogenically enhanced N and P loading, nutrient loading dynamics in most regions have changed radically over the past four decades (Vitousek et al. 1997; Boesch et al. 2001), with dramatic impacts on the structure and function of downstream ecosystems (Bricker et al. 1999; Elmgren and Larsson 2001; Diaz and Rosenberg 2008; Duarte et al. 2008). In response to the experimental evidence starting in the 1960s that P over-enrichment caused accelerated eutrophication in many lakes and reservoirs (Likens 1972; Schindler et al. 1973), P loading was restricted in many regions, starting with P removal in point source wastewater discharges, with notable desirable results (improvement of water quality on the North American Great Lakes, Lake Washington, Lake Erken, Sweden, Lake Geneva, Switzerland, Lake Biwa, and Japan). In contrast, N loading has increased in a more unabated fashion, in large part because N was not broadly identified as a limiting nutrient in freshwater ecosystems. However, studies in downstream estuarine and coastal ecosystems, beginning in the 1970s, showed many of these systems to be N-limited (Ryther and Dunstan 1971; Hobbie 1974; Hobbie and Smith 1975; D'Elia et al. 1986; Fisher et al. 1988; Elmgren and Larsson 2001). Furthermore, these studies identified the potential eutrophying threat that accelerating N loading could pose (Ryther and Dunstan 1971; D'Elia et al. 1986), a prediction applicable to coastal systems worldwide, where increased frequencies and geographic expansion of harmful algal blooms, hypoxia, habitat degradation, and fisheries losses have been closely linked to increases in N loading (c.f. Paerl 1988, 1997; Boesch et al. 2001; Rabalais and Turner 2001; Diaz and Rosenberg 2008).

There is irrefutable evidence that anthropogenically driven N loading events in estuarine and coastal waters have accelerated primary production, ultimately translating into organic matter enrichment with major negative biogeochemical consequences, including algal blooms, hypoxia, and altered food web structure and function (c.f. Nixon 1995; Boesch et al. 2001). Two widely cited examples include the large spring phytoplankton blooms

in Chesapeake Bay (Fisher et al. 1999; Boynton and Kemp 2000; Harding et al. 2002) and the Mississippi discharge region of the northern Gulf of Mexico (Lohrenz et al. 1997; Rabalais 2002) that are largely the result of N-enriched "freshets". However, N-driven eutrophication, caused by either expanding diffuse nonpoint and/or point source discharges, has also been thoroughly documented in many other geographically diverse estuarine and coastal systems, including regions of the North Sea; Mediterranean Sea and Baltic Sea (European Environmental Agency 2001; OSPAR 2008; Elmgren and Larsson 2001); Danish and Swedish fjords (Conley 2000; Elmgren and Larsson 2001); the Po River Delta (North Adriatic Sea) (Vollenweider et al. 1992); the Nile River Delta (Nixon 2004); The Pearl River Delta, Hong Kong (Yin et al. 2001); Mobile Bay, Alabama (Lehrter 2008); Tampa Bay, Florida (Greening and Janicki 2006); tributaries of the Chesapeake Bay (D'Elia et al. 1986); and the estuaries of the Pamlico Sound system, North Carolina (Hobbie 1974; Paerl et al. 1998, 2004).

Nitrogen-driven estuarine and coastal eutrophication has been, to some extent, exacerbated by P input constraints without accompanying N reductions in upstream lake and river systems, because the reduction in freshwater plant production in response to exclusive P input constraints has reduced the biomass that would otherwise have "filtered" N loads on their way to downstream N-sensitive estuarine and coastal waters (Elmgren and Larsson 2001; Paerl et al. 2004; Kronvang et al. 2005) (Fig. 3). Conversely, excessive N loading in some watersheds (e.g., Mississippi River watershed) has increased the potential for periodic P limitation in receiving coastal waters (Sylvan et al. 2006). Two lessons have been learned from these experiences: (1) nutrient limitation and its impacts on eutrophication need to be evaluated along the entire freshwater–marine continuum and (2) single nutrient input reductions (either N or P) are not likely to be effective in the wake of human modification of nutrient loading in watersheds discharging to the continuum. For these reasons, more recent efforts at stemming estuarine and coastal eutrophication have focused on carefully formulated dual nutrient (N and P) reductions (e.g., Neuse River Estuary, Chesapeake Bay, Baltic Sea, North Sea, Danish Fjords, and Northern Gulf of Mexico). In many respects, the dual nutrient approach represents an evolutionary step in arresting eutrophication, with the consideration of the larger scale freshwater–marine continuum being the driving force (Elmgren and Larsson 2001;

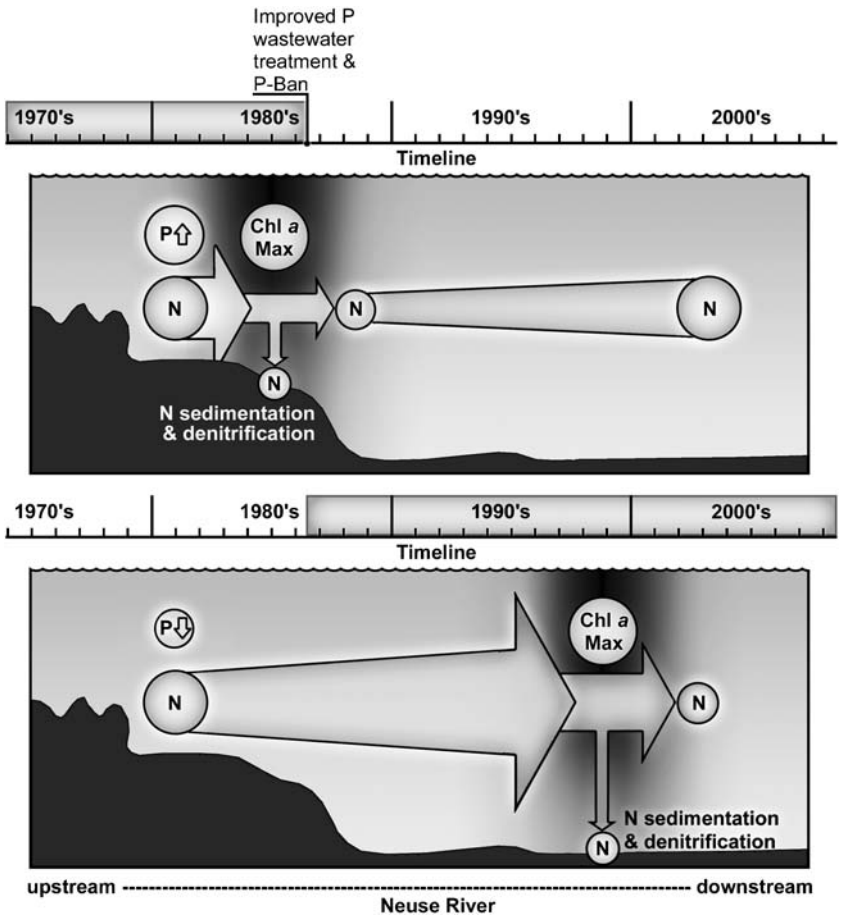

Fig. 3 Conceptual diagram showing the estuarine N filter effect of upstream P limitation on downstream N limitation for the Neuse River Estuary, NC, USA. Prior to P reductions in the 1980s, phytoplankton biomass was concentrated (shaded region) in the upstream oligohaline portion of the estuary (*upper frame*). This upstream biomass maximum acted as a "filter" (through N incorporation, sedimentation and denitrification) for N removal, thereby ensuring strong N limitation of downstream N-limited phytoplankton populations. Following P (but not N) removal in the mid to late 1980s, upstream P-limited phytoplankton biomass was reduced. However, this also reduced the upstream N filtering effect, allowing more N to travel downstream. Meanwhile, the N load increased due to increased anthropogenic N loading. The P-only reduction strategy led to enhancement of downstream N-controlled phytoplankton blooms (shaded region). Figure adapted from Paerl et al. (2004)

Paerl et al. 2004). Only focusing on a stream, lake, or river within this hydrologic continuum may at best only solve part of the larger scale eutrophication problem and at worst aggravate downstream ecological conditions.

The question naturally arises: why does not N_2 fixation compensate for N requirements in all ecosystems along the continuum? The answer to this question requires consideration of environmental factors potentially controlling this process that go far beyond the stoichiometric N/P ratio arguments (i.e., low N/P ratios, especially those below 5 will favor dominance by N_2 fixers) presented by Schindler et al. (2008) and others before (Doremus 1982; Tyrell 1999). Nitrogen fixation is an anaerobic process, which evolved in prokaryotic microorganisms before Earth had an oxygen-rich atmosphere (Knoll 2003). As such, microbes conducting this process, including photosynthetic bacteria, cyanobacteria, and a range of chemolithitrophic and heterotrophic bacteria, require oxygen-free conditions. These conditions can be provided in deoxygenated bottom sediments, biofilms, and locally anoxic aggregates and in the bottom hypoxic/anoxic waters of well-stratified, productive ecosystems (Paerl 1990). Some filamentous cyanobacterial genera, including those referred to by Schindler et al. (2008), are capable of conducting N_2 fixation under ambient oxic conditions, by confining the process to special oxygen-free cells called heterocysts. Heterocystous species are favored by calm, vertically stratified waters, where they can adjust their buoyancy and form aggregates that enable them to grow and fix N_2 under optimal conditions (Paerl et al. 2001), conditions experienced in Lake 227 during mid-summer, N-depleted periods.

Appreciable turbulence, as wind and/or tidal mixing, introduces small-scale shear that can disrupt aggregates and filaments, leading to decreased rates of N_2 fixation and even destruction and death of filaments and cells (Moisander et al. 2002a). Extensive vertical mixing also forces these diazotrophs to compete with non-diazotrophic phytoplankton, with the latter type often prevailing due to superior nutrient uptake and growth rates (Reynolds 2006). Estuarine and coastal waters are generally exposed to wind and tidal mixing throughout much of the year, rendering these waters suboptimal for N_2 fixation (Paerl and Zehr 2000; Paerl et al. 2001). Despite these constraints, some heterocystous species (e.g., *Nodularia* spp., *Aphanizomenon* spp, and *Anabaeana* spp.) as well as buoyant non-heterocystous species (*Trichodesmium* spp.) are able to take advantage of periods of calm, relatively warm, vertically stratified conditions in some coastal and even open ocean environments. Examples include the Baltic Sea and some tropical and subtropical ocean systems (Kononen et al. 1996; Karl et al. 2002; Paerl and Fulton 2006). However, even under these conditions, much less than the total N requirement of the whole phytoplankton community or ecosystem is met by N_2 fixation, in part because physically favorable conditions are ephemeral and highly seasonal (Paerl et al. 2001; Howarth and Marino 2006). Large, highly exposed lake systems likewise have these environmental constraints.

There are additional reasons why N_2 fixation may not be able to operate at optimal rates in N-limited systems, especially those away from land masses. These include deficiency of metals required for the synthesis and activity of the nitrogenase enzyme complex mediating this process, most notably iron (Fe). For example, nitrogenase activity in the widespread subtropical/tropic marine diazotroph, *Trichodesmium*, was shown to be Fe-limited at times in the Western Atlantic Ocean (Paerl et al. 2004). Interestingly, the bioassays used to determine Fe limitation showed P sufficiency at the time, although at other locations (e.g., North Central Pacific and Western Atlantic) P limitation may at times be operative. In addition, selective grazing could exert top-down controls on N_2-fixing microorganisms, reducing their influence on ecosystem-level N inputs and budgets (Howarth and Marino 2006).

In and of itself, salinity is not a barrier to the presence or proliferation of N_2 fixers (Moisander et al. 2002b). There are diverse marine analogs to the freshwater heterocystous and non-heterocystous diazotrophs. However, many of these analogs observed in N-deficient marine waters are associated with sediments, higher plants (e.g., marsh- and seagrasses), biofilms, and reefs. These are sites of protection from high degrees of turbulence and mixing, and they are relatively rich sites of macro- and micronutrients needed to support N_2 fixation (Paerl 1990). It is therefore concluded that the overall paucity of N_2 fixation and resultant persistent N limitation in marine waters can be attributed to many factors in addition to P limitation.

There are numerous additional reasons to warrant reducing N loading as a means of controlling eutrophication along the freshwater to marine continuum. Some of the most serious and detrimental symptoms of eutrophication along this continuum can be attributed to excessive N loading. These include toxin-producing blooms of non-N_2-fixing cyanobacteria, most notably the buoyant planktonic scum-former *Microcystis* and filamentous planktonic *Planktothrix*, as well as filamentous benthic genera such as *Lyngbya* and *Oscillatoria* in freshwater and oligohaline habitats, while downstream mesohaline to euhaline waters are more often dominated by eukaryotic bloom taxa, including dinoflagellates, diatoms, cryptophytes, chrysophytes, and prymnesiophytes. In many instances, recent blooms of these nuisance taxa can be attributed to excessive N loading (Granéli and Turner 2008; Paerl 1997; Paerl and Fulton 2006). Only reducing P inputs to systems impacted

by these blooms will not solve the eutrophication problem, certainly not in the short term, because the high levels of productivity and organic carbon production promoted by excessive N loading will stimulate "internal" nutrient recycling of P. In effect, excessive N loading makes P more available. In large lake, reservoir, river, and estuarine and coastal systems that have experienced a long history of either natural or anthropogenic P enrichment, N input reductions can be a highly effective way of reducing overall ecosystem productivity/eutrophication, while enabling the system to gradually "wean" itself of stored P.

Concluding Remarks

In conclusion, when one looks beyond the single system interpretation of nutrient limitation and related eutrophication dynamics to the entire freshwater to marine continuum, it turns out that P limitation is only part of the story. It is essential that we examine and evaluate nutrient limitation and its effects on this larger continuum scale because natural and human influences that affect upstream waters can have significant and adverse consequences on downstream waters, especially if they differ in the nutrient(s) that control production and nutrient cycling. There appear to be important inter-nutrient feedbacks operating when single nutrient reductions are imposed on a component of this continuum; these can have negative impacts on downstream estuarine and coastal waters. Recent experiences increasingly point to the importance and long-term efficacy of dual, as opposed to single, nutrient reduction strategies as a means of controlling eutrophication along the entire continuum.

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